STUDIES TO UNDERSTAND THE INFLUENCE OF MORPHOLOGY ON SEMICONDUCTOR/ELECTROLYTE INTERFACE IN PHOTOELECTROCHEMICAL SPLITTING OF WATER

A SYNOPSIS OF PROPOSED WORK SUBMITTED FOR
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1. INTRODUCTION

1.1. NEED FOR ALTERNATIVE ENERGY SOURCES

The backbone of civilization is our energy system, which facilitates the advancement of technology and in turn a higher standard of living. As per the recent estimates, 20 terawatts of carbon free energy will be needed by 2050 for maintaining the global energy supply[1]. Conventional sources of energy like petroleum, natural gas and coal etc. which meet most of the world's energy demand today are limited. The continuous use of fossil fuels create well known hazards which threaten human health and are associated with global climate change, such as the greenhouse effect, ozone layer depletion, acid rain and pollution. Therefore, there is an urgent need of alternative fuel which can fulfill the excessive and ever increasing demand of energy which is not only sustainable but is also ecofriendly.

1.2. Hydrogen: The fuel of the future

In the quest for new energy sources, hydrogen stands out as an attractive alternative energy carrier on account of the properties listed below:

- Hydrogen has high heat of combustion (34.18 kcal/g for H_2 and 10.30 kcal/g for petroleum)
- Energy released from hydrogen is 140 kJ/g while that of methane is only 33 kJ/g
- Energy storage capacity/mole of H_2 is 119 kJ/g while that of oil is 40 kJ/g
- It produces water upon combustion
- It is a renewable fuel
- It can be stored in gaseous, liquid or metal hydride forms
- It can be transported over large distances through pipelines or via tankers
- It can be converted into other forms of energy in more ways and more efficiently than any other fuel
- It is environmentally compatible since its production, storage, transportation and end products do not emit any greenhouse gases

1.3. Methods for production of hydrogen

In nature, hydrogen is not present in a gaseous form. However, it is abundant in plants, many hydrocarbons and water. Hence, hydrogen can be extracted from these compounds[2].

There are various methods and technologies for production of hydrogen. These technologies can be broadly classified as:

Non- Renewable methods

Thermal Processes

- Steam reforming process-
- Production of hydrogen from methane. It results in the emission of CO_2
- Gasification-
- Production of hydrogen from coal. It also emits CO_2

Electrolytic Processes - Production of hydrogen using electricity

Renewable methods involving solar energy

Photolytic Processes - Production of hydrogen using solar radiations

- Photobiological Water Splitting
- Photocatalytic Water Splitting
- Photoelectrochemical Water Splitting

1.4. Photoelectrochemical water splitting for solar hydrogen generation

Photoelectrochemical water splitting technology is analogous to photosynthesis. In photosynthesis, plants utilise sunlight, water, and carbon dioxide and convert them into carbohydrates and oxygen. In case of PEC technology, an electrochemical cell uses solar radiations to split water into hydrogen and oxygen. It replicates the natural process of photosynthesis and is also at times referred to as "Artificial Photosynthesis".

It is the most promising technology for hydrogen production because of the following reasons[2]:

• PEC technology is based on solar energy, which is a perpetual source of energy, and water, which is also a renewable resource

• PEC technology is environmental friendly technique with no undesirable by products

• PEC technology can be used on both large and small scales

• PEC technology is relatively uncomplicated

A typical photoelectrochemical cell, as depicted in **Fig. 1.1** for water splitting, consists of three electrodes immersed in an electrolyte solution; namely the working electrode (WE) or anode, counter electrode (CE) or cathode, and reference electrode (RE). The working electrode, usually a semiconductor, is also called the photoelectrode or photoanode due to the light induced chemical reactions initiated at its surface. The counter electrode or cathode used for this cell is typically a corrosion resistant metal, commonly platinum, to prevent dissolution products from the counter electrode contaminating the solution.

When a semiconductor with the right set of properties is immersed in an aqueous electrolyte and solar radiations are incident on it then, the solar energy is converted into electrical energy, which is directly used to split water into hydrogen and oxygen (chemical energy).

There are three possible assemblies for the arrangements of photo-electrodes[3]:

- photo-anode made of n-type semiconductor and cathode made of metal;
- photo-anode made of n-type semiconductor and photo-cathode made of p-type semiconductor;
- photo-cathode made of p-type semiconductor and anode made of metal

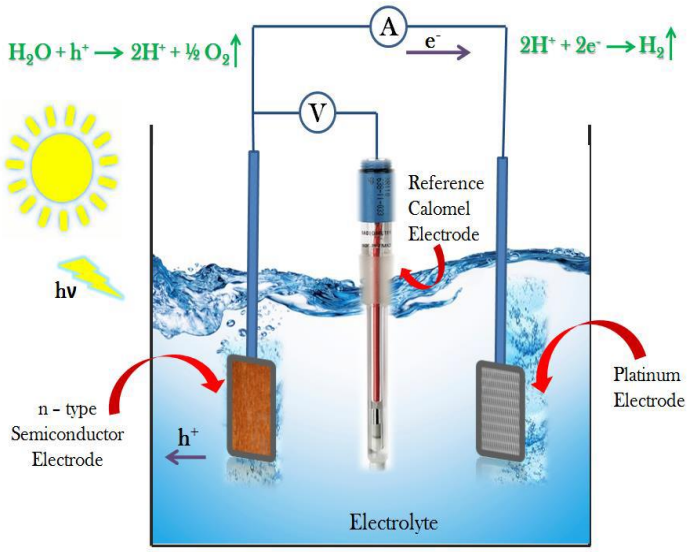


Fig.1.1 Schematic representation of a photoelectrochemical cell

When a semiconductor electrode is illuminated with photons having energy (hν) equal to or larger than the semiconductor band gap, the result is formation of electronic charge carriers, electrons in the conduction band and holes in the valence band. At the interface between the photoelectrode and electrolyte, the photogenerated holes (h^+) react with hydroxyl ions (OH^-) of water to form oxygen (O_2). Hence, gaseous oxygen is evolved at the photoelectrode. At the same time the photogenerated electrons are transferred through the external circuit to the cathode and react with hydrogen ions (H^+) at the cathode - electrolyte interface reducing the hydrogen ions to gaseous hydrogen (H_2).

These basic steps occurring in the photoelectrochemical cell can be summarized as below[4]:

1. **Photon absorption and charge carrier generation**

   Solar photons are absorbed by the semiconductor which create excited charge carriers in the form of electron- hole pairs.

   $$2h\upsilon \longrightarrow 2e^- + 2h^+$$

2. **Charge separation and transport**

   Photoexcited electron hole pairs are separated spatially and are transported to the surface.

3. **Oxidation of water by holes**

   Holes combine with the hydroxyl ions of water to produce oxygen gas.

   $$2h^+ + H_2O \longrightarrow ½\ O_2\,(g) + 2H^+ \qquad \text{——} \qquad (1)$$

4. **Reduction of H^+ ions**

   The majority charge carriers i.e. electrons are drifted towards the metal electrode (typically Pt) where they combine with H^+ ions in the electrolyte solution to produce H_2 gas which completes the reaction.

   $$2e^- + 2H^+ \longrightarrow H_2\,(g) \qquad \text{——} \qquad (2)$$

   The overall reaction can be written as:

   $$2h\nu + H_2O \longrightarrow H_2\,(g) + ½\ O_2\,(g) \qquad \text{——} \qquad (3)$$

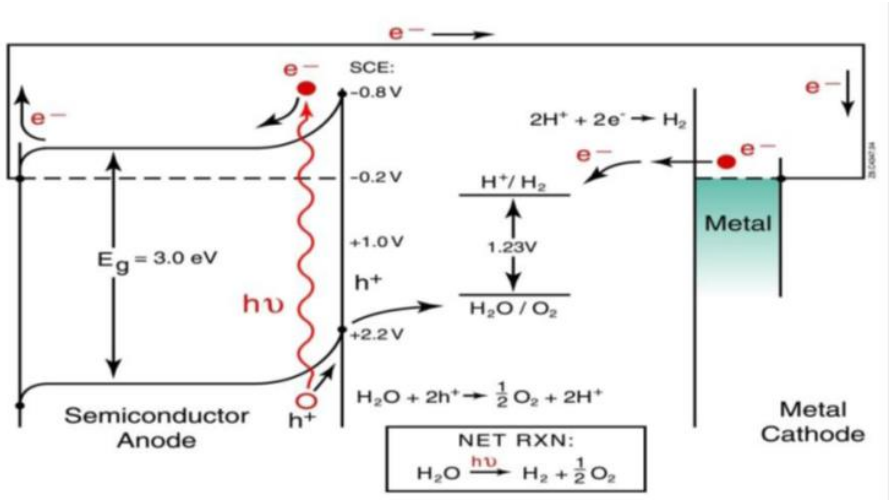


Fig.1.2. Working Principle of Photoelectrochemical Cell for Water Splitting

The Standard Gibbs free energy of the reaction is 237.2 kJ /mol.

$$\Delta E° = \Delta G°/ nF$$

$$= -1.23 \text{ V}$$

Where, ΔE° is the standard potential, n (=2) is the number of electrons exchanged, F is the Faraday constant.

For Oxidation:

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

$$E_{ox}° = 1.23 \text{ V } vs. \text{ SHE} \quad \text{—— (4)}$$

For Reduction:

$$2H^+ + 2e^- \longrightarrow H_2$$

$$E_{red}° = 0.00 \text{ V } vs. \text{ SHE} \quad \text{—— (5)}$$

Overall Reaction:

$$2H_2O \longrightarrow O_2 + 2H_2$$

$$\Delta E° = -1.23 \text{ V} \quad \text{—— (6)}$$

For the reaction to proceed 1.23 V must be provided externally. At standard temperature (298 K) and concentrations (1 mol/L, 1 bar), the electrochemical cell voltage ΔE of-1.23 V corresponds to a Gibbs free energy change of +237 kJ/mol H_2. This indicates that the water-splitting reaction is thermodynamically non-spontaneous reaction. There are energy losses caused by the recombination of the photogenerated charge carriers (-0.8 eV), resistance of the

electrodes and electrical connections, voltage losses at the contacts etc. Hence, voltage of about 1.6-2.0 eV is needed for spontaneous water splitting[5,6].

The performance of photoelectrochemical cells can be evaluated in terms of [2]:

• Generation and excitation of electron–hole pairs in photo-electrodes

• Separation of electron- hole pairs in photo-electrodes

• Generation of the sufficient voltage required for water decomposition

• Electrode processes and related charge transfer within photoelectrochemical cells

1.5. The Heart of PEC system: Semiconductor Electrode

The efficiency with which the splitting of water is carried out by a photoelectrochemical cell is determined principally by the performance of the materials used for photo-electrodes. Semiconductor working electrode therefore is the heart of photoelectrochemical cell as it drives the process of splitting of water. During the last more than three decades various metal oxides (TiO_2, $SrTiO_3$, Fe_2O_3, Cu_2O etc.)[7] and non-oxides (GaAs, CdS, InP, etc.) semiconductors have been employed as photoanodes in photoelectrochemical cells. To achieve efficient splitting of water, the semiconductor photoanode should meet the following criteria[2,6,8-9]:

An ideal photoanode should

- have conduction band edge more negative than the H_2 evolution potential and valence band edge more positive than the O_2 evolution potential
- absorb light from a substantial part of the solar spectrum efficiently
- offer high surface area for maximum absorption of sunlight
- have band gap between 1.6–2.0 eV
- effectively utilize the absorbed energy to produce maximum electron-hole pairs
- facilitate rapid transport of the charges
- be corrosion resistant
- be inexpensive and easily available
- be stable in the electrolyte for a long time
- durability > 2000 hours
- solar to hydrogen conversion efficiency (STH) > 10%

Several metal oxide semiconductors have been and are being used as photoelectrodes in photoelectrochemical water splitting for hydrogen generation. After the pioneering work of Fujishima and Honda in 1972 who worked with TiO_2 as the semiconductor electrode, attention of several investigators is now directed towards other metal oxides such as:

Materials with High band gap:

They are poor harvesters of solar radiations and do absorb in the UV region of light, but exhibit high stability in aqueous electrolytes.

e.g. TiO_2, WO_3, $SrTiO_3$, $BaTiO_3$, SnO_2, ZnO

Materials with Low band gap:

They are good harvesters of solar radiations but exhibit poor stability in aqueous electrolyte.

e.g.: Si, GaAs, InP, CdTe, CdSe, CuO.

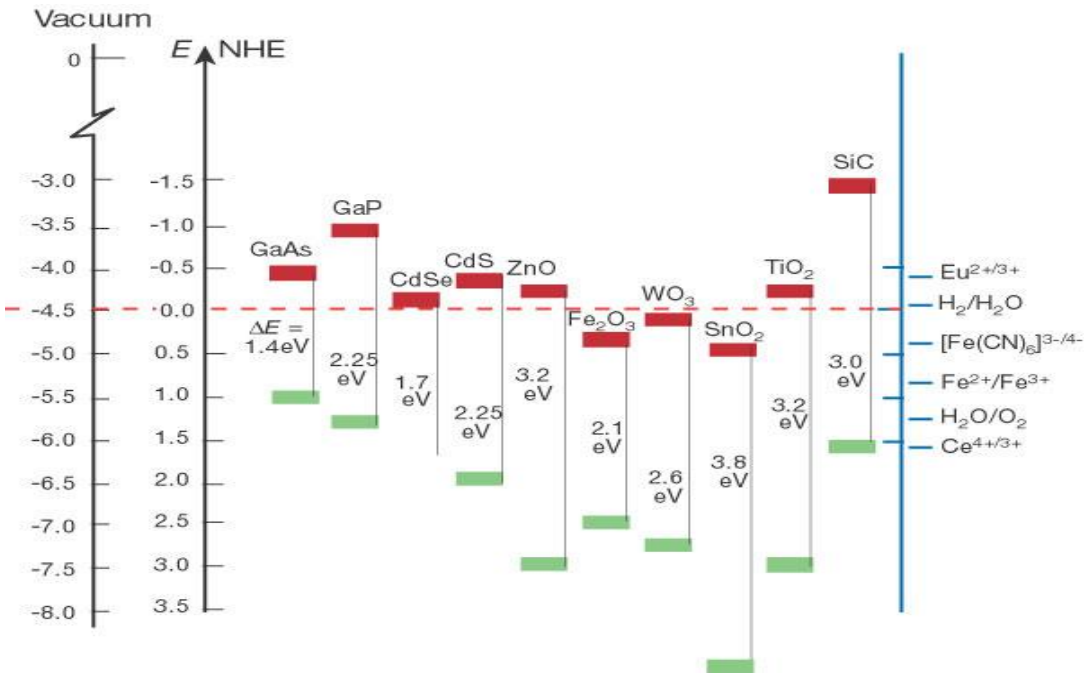


Fig.1.3.Band positions of several semiconductors in contact with aqueous electrolyte at pH 1[10]

Though world over researchers are involved in developing the ideal semiconductor with the above said properties but so far the success has eluded them and the search for an ideal semiconductor is far from over.

1.6. Gap in the existing knowledge: The Semiconductor/Electrolyte Interface

Research on photoelectrochemical water splitting is focused on increasing the efficiency of hydrogen generation and various modification strategies are being tried on different semiconductors viz. doping, swift heavy ion irradiation, dye sensitization, heterojunctions etc. Semiconductors are rightly considered as the centre of research for hydrogen generation but, equally important is the semiconductor electrode/electrolyte interface, a site where electrochemical reactions takes place that are responsible for photoelectrochemical splitting of water. At the interface electron-hole pair generation and separation take place and therefore the study of interface is very important for elucidation of mechanism of photoelectrochemical water splitting.

It is also important to mention that morphology of the electrode under study plays an important role in electron- hole pair generation and its further movement. Inspite of the fact that a lot of work is being carried out in this important area of semiconductor development and modification, limited studies are available on morphologies of electrode/electrolyte interface with respect to photoelectrochemical water splitting and therefore this area requires special focus and investigation.

Research focusing on the energy and charge transfer phenomena at the illuminated semiconductor–liquid interface was pioneered by Marcus in 1956[11] and has considerably progressed over the decades. Electrochemistry at the semiconductor–liquid interface is often discussed in terms of the Marcus–Gerischer model which refers to ideal direct charge transfer. Studies on semiconductor/electrolyte interface in photoelectrochemical cells has become an area of interest as it can provide insight into the charge transport phenomenon[12].

1.7. Semiconductor/Electrolyte interface

When a semiconductor is partly immersed in an electrolyte, a potential is set up across the two phases, i.e., at the electrode/electrolyte interface. The more common terminology in electrochemistry is that a *double layer* is set up at the interface. It was Von Helmholtz in 1853, who proposed the first type of model for the structure of the double layer at the electrode/electrolyte interface. It is analogous to that in a solid-state capacitor, i.e., two layers of charge of opposite sign are separated by a fixed distance[13].

The double layer is usually divided into two regions: the compact double layer (referred to as the Helmholtz double layer) situated between the electrode and the surface of the closest approach and the diffuse double layer extending from the surface of the closest approach to the bulk of the solution.

Various models of the electrical double layer have been developed by different researchers. However, the most accepted model of the electrical double layer was given by Bockris, Devanathan and Muller in 1963[14].

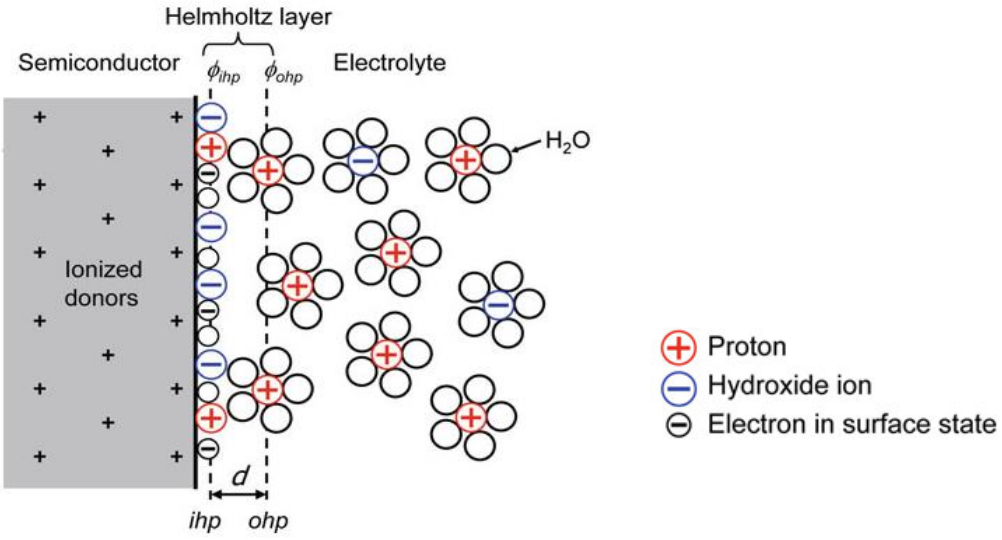


Fig.1.4. Electrochemical double layer showing inner Helmholtz layer, outer Helmholtz layer and Diffuse layer[5]

The charged species such as electrons, holes or immobile impurity ions contribute to the potential distribution across the electrical double layer. The potential drops exponentially from the inner helmholtz layer to the diffuse layer.

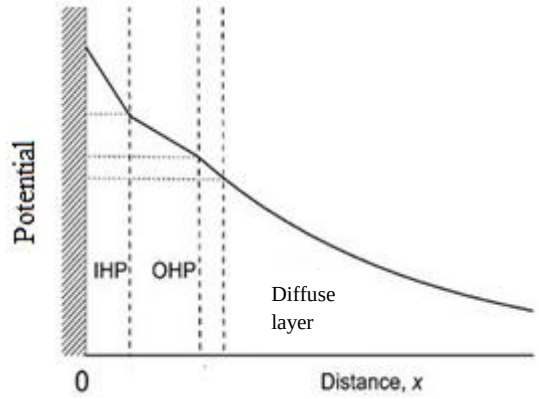


Fig.1.5. Variation of potential across the electrical double layer

The layers act as capacitors in series. Hence, the equivalent circuit for the semiconductor/electrolyte interface can be represented as two capacitors in series and the overall capacity can be expressed as[15]:

$$\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_{DI}}$$

Where, C_H is the capacitance of Helmholtz layer and C_{dl} is the capacitance of diffuse layer.

1.8. Electrode Morphology and Impedance Response

It has been observed that the impedance of an electrode depends on the morphological disorders of the surface, viz., ***roughness and porosity***[16].

Solid electrodes are not smooth, but have complex surface morphology with varying degree of irregularities. Fractal models are used in order to study the effect of surface irregularities (roughness, porosity etc. which can explain the effect of electrode transfer on electrochemical response[17]

i. Influence of Roughness

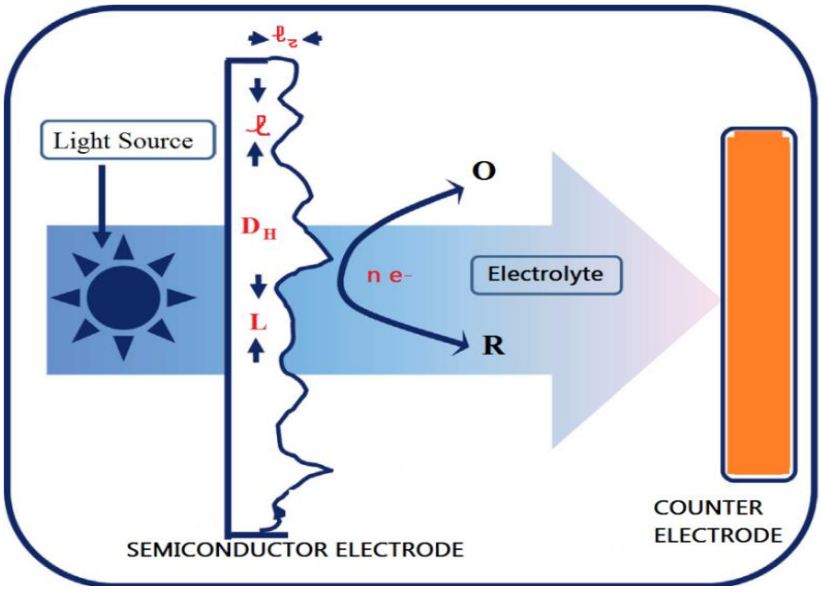


Fig.1.6. Schematic representation of an arbitrary rough fractal electrode undergoing charge transfer having fractal dimension (D_H), lower cut-off length scale (ļ), upper cut-off length scale (L) and width of the interface ($ļ_\tau$)[18]

Fig. 1.6. depicts the rough electrode/electrolyte interface with fractal morphological parameters that control the electrochemical responses. The power spectrum of such rough electrode/electrolyte interfaces obtained from AFM and SEM image analysis consists of four morphological characteristics, including the fractal dimension (D_H), the lower (ļ) and upper (L) cut-off length scales of fractality and the strength of fractality(μ). Only three of these characteristics (D_H, ļ and μ) contribute strongly to the electrochemical response of the electrode while L contributes weakly. The increase in the strength of fractility (μ) or decrease in the lower cut-off length scale (ļ) increases the roughness[19].

ii. Porosity

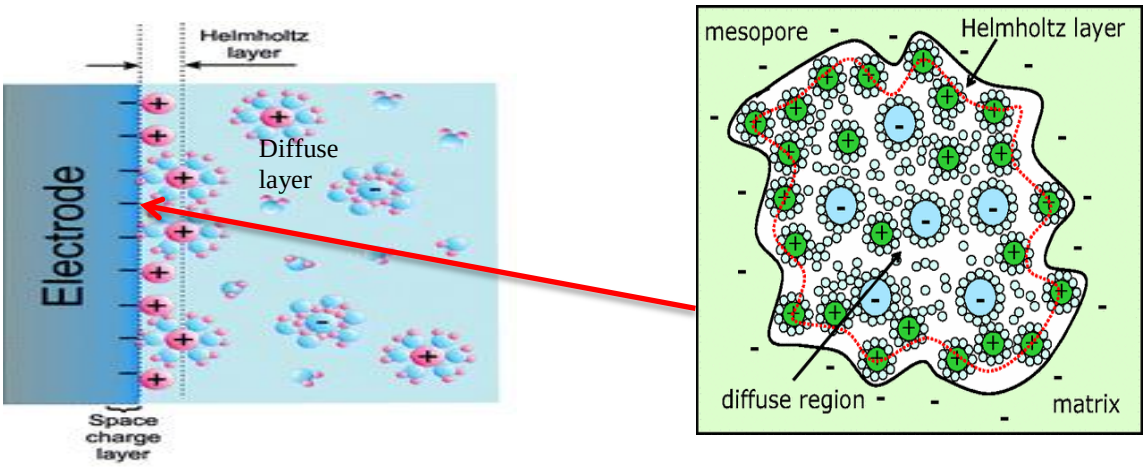
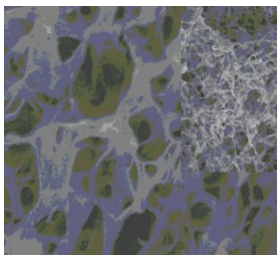
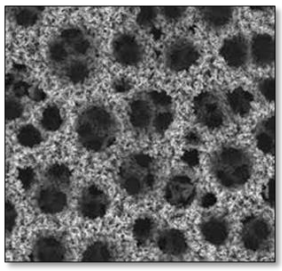


Fig.1.7. Schematic model of the electrical double layer formed in an arbitrary nanoporous electrode showing the Helmholtz layer and the diffuse layer[20]

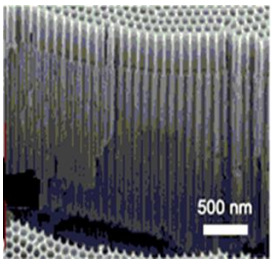
The morphology of nanoporous and mesoporous electrode materials strongly influence the electrochemical impedance. The pore structures with interconnected three-dimensional connectivity of non-uniform shape and size create complexity in the electrode surface. The morphology of the pores may be prolate, oblate, ellipsoidal, spheroidal, tubular, etc.



ELLIPSOIDAL PORES



SPHERICAL PORES



TUBULAR PORES

The forms and morphologies of these pores can be easily identified by their local curvatures[20]. The geometry and the morphology of these pores also affect the electrochemical response of the electrodes.

MOTIVATION OF THE PRESENT WORK

It becomes clear from the above discussion that the present work is an attempt to study the influence of morphology on the semiconductor/ electrolyte interface in photoelectrochemical splitting of water. The results of the present study are expected to bring out the hitherto unknown mechanism at the interface and would also contribute in developing more efficient electrodes for use in photoelectrochemical splitting of water.

2. LITERATURE SURVEY

While there are voluminous reports available in photoelectrochemical splitting of water[3,21-29], a brief review of literature in the field of semiconductor/electrolyte interfaces and photoelectrochemical systems in recent years is given below:

- **S. Srinivasan[13] (2006)** explained the structure, charge and capacitance characteristics of electrical double layer formed at the semiconductor/ electrolyte interface. Various models of electrical double layer proposed by different researchers are explained in detail. Structures of semiconductor/electrolyte and insulator/electrolyte interfaces are also analyzed in the paper.
- **R. V. Krol[5] et al (2012)** have explained the basic concepts of photoelectrochemical cells along with the formation of double layer and process of interfacial charge transfer. Information on the role of surface states in interfacial charge transfer and fermi level pinning is also discussed.
- **M. F. Lichterman[30] et al (2015)** used Operando ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) to directly characterize the semiconductor/liquid interface at room temperature under real-time electrochemical control. X-ray synchrotron radiation in conjunction with AP-XPS has enabled simultaneous monitoring of the solid surface, the solid/electrolyte interface, and the bulk electrolyte of a photoelctrochemical cell as a function of the applied potential,

U. The observed shifts in binding energy with respect to the applied potential have directly revealed ohmic and rectifying junction behavior on metallized and semiconducting samples, respectively.

- **C. A. Grimes**[31] **et al (2008)** have provided information on the generation of solar hydrogen by photoelectrochemical water splitting. Origin of electrical double layer and the mechanism of charge carrier transfer across the semiconductor/electrolyte interface have also been explained.
- **B. Zhang**[32] **et al (2016)** investigated the fast charge transfer kinetics at the photoelectrode/electrolyte interface for efficient photoelectrochemical water splitting system by scanning electrochemical microscopy (SECM) in the feedback mode in order to simulate the oxygen evolution process in PEC system. $BiVO_4$ and Mo doped $BiVO_4$ (labeled as Mo:$BiVO_4$) were selected as photoanodes and the common redox couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ as molecular probe. After excitation the ratio of rate constant for photogenerated hole to electron via Mo:$BiVO_4$ reacting with mediator at the electrode/electrolyte interface was found to be about 30 times larger than that of $BiVO_4$. This suggested that introduction of Mo^{6+} ion into $BiVO_4$ can possibly facilitate solar to oxygen evolution (hole involved process) and suppress the interfacial back reaction (electron involved process) at photoanode/electrolyte interface.
- **Y. T. Law**[33] **et al (2015)** used in situ techniques to probe the structure and the composition of the dynamic electrode/electrolyte interfacial region. This work demonstrated the potential of the near ambient pressure X-ray photoelectron spectroscopy (NAPXPS) for in situ studies of processes occurring at the interface between a metal electrode and a liquid electrolyte. By using a model membrane electrode assembly of a high temperature phosphoric acid-imbibed proton exchange membrane fuel cell, and combining NAPXPS measurements with the density functional theory, it was possible to monitor such fundamental processes as dissociation and migration of the phosphoric acid within a nanostructured Pt electrode under polarization.

- **R. Kant and M. B. Singh**[20] **(2013)** generalized the linearized Gouy-Chapman-Stern theory of an electric double layer for morphologically complex and disordered electrodes. The effect of the surface morphology of an electrode on an electric double layer was obtained using multiple scattering formalism in surface curvature. It also includes the contribution of compact layer in the overall prediction of capacitance. The theory showed the presence of geometrical fluctuations in porous systems causing an enhanced dependence of capacitance on mean pore sizes and suppresses the magnitude of capacitance.
- **L. Larina**[34] **et al (2008)** analyzed the role of interfacial bandgap states in sub-bandgap photoinduced electron transfer across a ZnO/electrolyte junction using time-resolved photocurrent measurements in the millisecond regime. The crystallographic structure and morphology of ZnO samples were characterized using X-ray diffraction and scanning electron microscopy measurements. A kinetic model for charge-carrier transport at the ZnO/electrolyte interface based on the intermediacy of the surface states was developed and the rate equations were analytically solved. Based on an analysis of the experimental data and theoretical predictions, the density of the surface states was determined to be 3.1 X 10^{13} cm^{-2} and the capture cross section area was found to be 1.5 X 10^{-16} cm^2.
- **C. A. Koval and J. N. Howard**[35] **(1992)** explained the interfacial electron transfer with the help of basic models for electron transfer. The theory for charge transfer under dark and illumination, different types of semiconductor/electrolyte interfaces, various techniques for investigations of semiconductor/electrolyte interfaces etc. have been discussed.
- **M. N. Latto**[12] **et al (2004)** considered the influence of surface chemistry and boron doping density important on the redox chemistry of $Fe(CN)_6^{3-/4-}$ at CVD polycrystalline diamond in determining the rate of charge transfer at the electrode/electrolyte interface. The electrochemical behavior of hydrogen terminated CVD diamond and oxygen terminated CVD diamond with doping density is compared. This was explained as surface state mediated charge transfer mechanism. This demonstrated the importance of controlling surface chemistry in electroanalytical applications.

- **S. Srivastav and R. Kant**[16] **(2011)** presented the theoretical results elucidating the influence of uncompensated solution resistance on anomalous Warburg's impedance. The mathematical expression which incorporated the diffusion at the rough electrode/electrolyte interface and bulk solution resistance was obtained. The roughness at the interface is contained in the expression through the surface structure factor, which is used to describe any random surface morphology statistically. Detailed analysis for realistic fractal electrodes, characterized as a finite self-affine scaling property with two lateral cutoff lengths is presented.
- **Md.M. Islam and R. Kant**[19] **(2011)** generalized the Anson equation for chronocoulometry at deterministic and randomly rough electrode/electrolyte interface morphologies by the power spectrum of roughness. An elegant mathematical formula between the surface roughness power spectrum and the charge transient was obtained. An increase in roughness increases the magnitude of charge transients, which introduce non-linear behavior in traditional Anson plots. This generalization provides insight into the effect of fractal and nonfractal morphological disorder on the chronocoulometric measurements of Nernstian charge transfer under the potential step method.
- **S. Dhillon and R. Kant**[17] **(2014)** developed a theory for the DPSC (double potential step chronoamperometry) response for finite fractal and nonfractal electrode roughness with and without uncompensated solution resistance. Mathematical equation for the statistically averaged current transient and its relation to surface structure factor of random roughness was highlighted for reversible charge transfer. The increase in the ratio of reverse and forward current was shown due to electrode roughness which is usually understood due to kinetic complications.

3. **PRESENT WORK**

The present work is proposed to be carried out on understanding the role of semiconductor electrode/electrolyte interface roughness on the photoelectrochemical water splitting for hydrogen generation vis-a-vis studying the influence of morphology of semiconductor electrodes prepared from different techniques. The photoelectrochemical technique for hydrogen generation has, to the best of our knowledge not been studied so far from the semiconductor/electrolyte interface point of view and the details about the influence of morphology on photoelectrochemical water splitting is still missing. Even after four decades of photoelectrochemical water splitting pioneer work by Fujishima and Honda in 1972, we have still not explored the detailed phenomena occurring at the complex interface. Thus, the understanding of the electrochemical phenomena at the rough semiconductor/electrolyte interface becomes very important in the research of photoelectrochemical water splitting to produce the fuel of the future: Hydrogen.

The study will be performed on Fe_2O_3, ZnO, Cu_2O etc. metal oxides as these metal oxides have been already investigated with respect to their application in photoelectrochemical splitting of water in our lab.They have shown significant photoresponse as their band gap is well aligned with redox potential of water, so they absorb maximum portion of solar spectrum. Also, they are chemically stable, cost effective and their method of preparation are well established. Study of these oxides in context to their electrode/electrolyte interface will add to the knowledge for increasing the efficiency of photoelectrochemical cells and this will open new channels for modification and innovation in the area of photoelectrochemical water splitting research.

4. OBJECTIVES OF STUDY

- Preparation of thin films of nanostructured metal oxides (viz. Fe_2O_3, ZnO, Cu_2O etc.) by
  - ✓ Sol gel method
  - ✓ Spray pyrolysis
  - ✓ Electrodeposition
  - ✓ RF Sputtering
- Characterization of thin films of metal oxide nanoparticles will be done by
  - ✓ XRD: To observe the formation of different phases and to estimate the average grain/ particle size using Scherrer's calculations.
  - ✓ SEM and AFM: To observe the surface morphology of the films.
  - ✓ UV- Visible Spectroscopy: To find the band-gap.
- Impedance analysis of the thin films under constant illumination by Electrochemical Impedance Spectroscopy (EIS)
- Morphological characterization of the used electrodes through Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM)
- Study of photoelectrochemical behavior of thin films of nanostructured metal oxides both in dark and under illumination at different electrolytic conditions (pH, conc. of electrolyte etc.) will be done for all samples
- To establish correlation between the experimental data with the results obtained using theoretical model (developed at Prof. Rama Kant's lab at Complex Systems Group, Dept. of Chemistry, University of Delhi) to study the effect of morphology of electrode on the charge transfer kinetics across semiconductor/electrolyte interface

5. PROPOSED METHODOLOGY

5.1. Preparation of samples: thin films

Nanostructured thin films will be grown by sol-gel method, spray pyrolysis, RF sputtering available at IUAC, New Delhi to produce thin films of different morphologies. Thin films of semiconductor materials would be developed on TCO or ITO conducting glass.

5.2. Characterization of thin films

Structure and Surface Morphology:

Structural analysis of the samples would be performed by X-ray diffraction technique to check the polycrystallinity of the compound formed and to confirm the formation of desired phase.

For determining surface morphologies such as, grain size (particle size), grain structure, surface roughness of the material. Fractal surface characterization would be done by SEM (scanning electron microscopy) and AFM (Atomic Force Microcopy) analysis.

The power spectra obtained from SEM and AFM image analysis using *Mathematica 8.0.1* software will provide information about morphological characteristics including the fractal dimension (D_H), the lower (l) and upper (L) cut-off length scales of fractality and the strength of fractality(μ) of the rough electrode surface. Hence, this measurement is expected to be a crucial part of the proposed study.

Particle size analysis:

The size of the particles within the range of nano dimensions plays a very important role in modifying the properties of the materials. Average particle size and crystal phase will be analysed through *Bruker AXS-D8 Advance* X-ray Diffractometer. Scherrer equation ($0.9\lambda/\beta\cos\theta$) will be employed to calculate the average particle size.

Film thickness:

Aplha step D-Tencor T120 (surface profilometer) available at Dayalbagh Educational Institute, Agra will be used to measure film thickness.

Resistivity:

Transverse resistance and thus, resistivity of the sample will be measured by resistance meter. Additionally current voltage characteristics would also be used for resistance measurement. For this purpose a large contact would be made on one side of sample while on the reverse side a small pressure contact would be used.

Bandgap:

Using *Tauc* plots, Eg will be determined by plotting ($\alpha h\nu$)1/2 vs. hν using the equation below:

Absorption coefficient, α = A (hν – Eg)1/2

The above calculation will be done by UV-Vis spectrophotometer (shimadzu, UV-2450) at Dayalbagh Educational Institute, Agra.

Mott-Schottky plot*:*

An LCR meter would be employed to measure capacitance (C) at semiconductor electrolyte junction. $1/C^2$ versus electrode voltage plot will give band bending, flatband potential and donor/acceptor densities with the help of following Mott-Schottky equation.

$$\frac{1}{C^2} = \left(\frac{2}{q\varepsilon_o \varepsilon N_D}\right)\left(V_{app} - V_{FB} - \frac{kT}{q}\right)$$

Where ε_o is the permittivity of the vacuum, N_D is the donor density, V_{app} is the applied potential, ε is the dielectric constant of the semiconductor, kT/q is the temperature dependent term.

5.3. Impedance analysis for understanding charge transfer kinetics across semiconductor/electrolyte interface:

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for investigating electrochemical systems and processes. Multiple parameters can be determined from a single Nyquist plot and Bode Plot.

Nyquist plot:

In Nyquist Plot, the diameter of the semicircle can be directly related to the charge transfer resistance at the solid/liquid interface, which signifies the polarization resistance of the used electrode to ions diffusion. It also gives the magnitude of solution resistance.

Bode plot:

The Bode plot gives the absolute impedance |Z| and the phase shift (θ) of the impedance, each as a function of frequency. Impedance of the thin films would be studied under constant illumination. Physical interpretation of various parameters of interfacial charge transfer processes obtained from Bode plot would help in understanding the charge transfer kinetics across the semiconductor electrode/electrolyte interface..

5.4. Photo electrochemical Studies

Photoelectrochemical measurements would be carried out on thin film samples as photosensitive working electrode, in conjunction with platinum as the counter electrode and saturated calomel electrode (SCE as reference electrode), at varying electrolyte conditions. Nature, pH and concentration of the electrolyte would also be varied in order to optimize the conditions for H_2 evolution. I- V characteristics of photoelectrochemical cell would be studied both under dark and illumination using *Zahner Electrochemical Workstation* and 300 W Xenon or Tungsten light source. By observing the I-V plots, onset voltage for photocurrent would be determined and based on these measurements the performance of photoelectrochemical cell would be evaluated.

5.5. Establishing correlation between the experimental data with the results obtained using theoretical model

Attempts will be made to correlate the data obtained from experiments with the results obtained using theoretical model for studying the morphological factors affecting the electrochemical response across the semiconductor electrode/ electrolyte interface. The results would be evaluated and conclusions would be derived for increasing the efficiency of hydrogen generation by photoelectrochemical splitting of water.

6. **REFERENCES**

1. A. J. Nozik, J.R. Miller, Introduction to Solar Photon Conversion; *Chem. Rev.*; 2010, 110(11), 6443–6445.
2. T. Bak, J. Nowotny, M. Rekas, C.C. Sorrell, Photo-electrochemical hydrogen generation from water using solar energy; *Int. J. of Hydrogen Energy*; 2002, 27, 991 –1022.
3. A. Fujishima, K. Honda, *Nature*, 1972, 283, 37-38.
4. E. L. Miller, Solar Hydrogen Production by Photoelectrochemical Water Splitting: The Promise and Challenge On Solar Hydrogen & Nanotechnology Edited by Lionel, John Wiley& Sons (Asia) Pte Ltd., 2009, 3-35.
5. R. V. Krol and M. Gratzel (eds.), Photoelectrochemical Hydrogen Production, *Electronic Materials: Science & Technology* 102, 2012, 13-67.
6. S. Choudhary, S. Upadhyay, P. Kumar, N. Singh, V.R. Satsangi, R. Shrivastav, S. Dass, Nanostructured bilayered thin films in photoelectrochemical water splitting- A review; *Int. J. of Hydrogen Energy*; 2012, 37(24), 18713-18730.
7. D. Sharma, Nanostructured SrTiO3 thin films sensitized by Cu_2O for photoelectrochemical hydrogen generation, *International Journal of Hydrogen Energy*, 39 (2014) 4189- 4197.
8. S. U. M Khan, J. O. M. Bockris, A model for electron transfer at the illuminated p-type semiconductor-solution interface, J. *Phys. Chem.*, 1984, 88, 2504-2515.
9. V. R. Subramanian, Nanostructured Semiconductor Composites for Solar Cells, *The Electrochemical Society Interface*, 2007, 16, 32-36.
10. M. Grätzel, Photoelectrochemical cells; *Nature*; 2001, 414, 338-344.
11. R. A. Marcus, *J. Chem. Phys*, 1956, 24, 966.
12. M. N. Latto, G. Pastor-Moreno and D. J. Riley, *Electroanalysis*, 2004, 16, 434–441.
13. S. Srinivasan, Electrode/Electrolyte Interfaces: Structure and Kinetics Of Charge Transfer, Fuel cells, Springer US, 2006, 27-92.
14. J. O'M. Bockris, M. A. V. Devanathan, K. Muller, On the structure of charged interfaces, *Proceedings of the Royal Society A: Mathematical, Physical & Engineering Sciences*, 1963, 274, 55-79.
15. A. J. Bard, L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley and Sons, New York, 1980.

16. S. Srivastav and R. Kant, *J. Phys. Chem. C,* 2011, 115, 12232–12242.
17. S. Dhillon, R. Kant, *Electrochimica Acta,* 129, (2014) 245–258.
18. R. Kant, Md. M. Islam, Theory of single potential step absorbance transient at an optically transparent rough and finite fractal electrode: EC mechanism, *Journal of Electroanalytical Chemistry*, 2014, 713, 82–90.
19. Md. M. Islam, R. Kant , Electrochimica Act, 2011, 56, 4467–4474.
20. R. Kant and M. B. Singh, Generalization of the Gouy-Chapman-Stern model of an electric double layer for a morphologically complex electrode: Deterministic and stochastic morphologies, *Physical Review E*, 2013, 88, 052303.
21. J. R. Bolton, and D. O. Hall, Photochemical Conversion and Storage of Solar Energy, *Annual Review of Energy*, 1979, 4, 353-401.
22. T. Inoue and T. Yamase, Photoelectrochemical cell using SiC for water splitting, *Chemistry Letters*, 1985, 14, 869-872.
23. Y. Sakai, S. Sugahara, M. Matsumura, Y. Nakato, H. Tsubomura, Photoelectrochemical water splitting by tandem type and heterojunction amorphous silicon electrodes, *Canadian Journal of Chemistry*, 1988, 66(8), 1853-1856.
24. D. Liu, P. V. Kamat, Photoelectrochemical behavior of thin CdSe and coupled TiO2/CdSe semiconductor films. *J Phys Chem*, 1993, 97, 10769-73.
25. C. Nasr, P. V. Kamat, S. Hotchandani, Photoelectrochemical behavior of coupled SnO2/CdS nanocrystalline semiconductor films. *J Electroanal Chem*, 1997, 420, 201-7.
26. S. Martirosyan, Streamlining CdSe/CdS PEC characteristics using Cd metal substrate. *Sol Energy Mater Sol Cells*, 2001, 70, 115-9.
27. S. Yamada, A. Y. Nosaka, Y. Nosaka, Fabrication of CdS photoelectrodes coated with titania nanosheets for water splitting with visible light. *J Electroanal Chem*, 2005, 585, 105-12.
28. C. Chi, Y. Lee, H. Weng, A CdS-modified TiO2 nanocrystalline photoanode for efficient hydrogen generation by visible light. *Nanotechnology*, 2008, 19(125704):5.
29. Z. Zhang, P. Wang, Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy. *J Mater Chem*, 2012, 22, 2456-64.

30. M. F. Lichterman, S. Hu, M. H. Richter, E. J. Crumlin, Direct observation of the energetics at a Semiconductor/liquid junction by Operando X- ray photoelectron spectroscopy, *Energy Environ . Sci*., 2015, 8, 2409-2416.
31. C. A. Grimes, O. K. Varghese, S. Ranjan, Light, Water, Hydrogen: The Solar Generation of Hydrogen by Water Photoelectrolysis, *Springer US, New York*, 2008
32. B. Zhang, X. Zhang, X. Xiao, Y. Shen, Photoelectrochemical Water Splitting System-A Study of Interfacial Charge Transfer with Scanning Electrochemical Microscopy, *ACS Appl. Mater. Interfaces*, 2016, 8, 1606−1614.
33. Y. T. Law, S. Zafeiratos, S. G. Neophytides, A. Orfanidi, D. Costa, T. Dintzer, In situ investigation of dissociation and migration phenomena at the Pt/electrolyte interface of an electrochemical cell, *Chem. Sci*., 2015, 6, 5635–5642 | 5635.
34. L. Larina, E. M. Trukhan, O. Shevaleevskiy, B. T. Ahna, Charge Transfer across a ZnO/Electrolyte Interface Induced by Sub-Bandgap Illumination: Role of the Surface States, *Journal of The Electrochemical Society*, 2008, 155 (7) H529-H535.
35. C. A. Koval, J. N. Howard , Electron Transfer at Semiconductor Electrode-Liquid Electrolyte Interfaces, *Chem. Rev*, 1992, *92*, 411-433.